

# Thermal Degradation of Carboxylate-Based Polyurethane Anionomers

Katsuji Matsunaga, Masahiro Tajima, Yasuhiko Yoshida

Department of Applied Chemistry, Faculty of Engineering, Toyo University, 2100 Kujirai, Kawagoe-shi, Saitama 350-8585, Japan

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**ABSTRACT:** With the purpose of elucidating the thermal degradation process of carboxylated polyurethane anionomers (PUAs), characterization of PUAs containing potassium and magnesium salts was conducted using thermogravimetry and FTIR spectroscopy. Potassium salt in PUA induced pronounced acceleration on the thermal degradation of urethane linkage in the hard segment as well as ester and carbonate linkages in the soft segment. The absorption bands of  $\nu(\text{N—H})$ ,  $\nu(\text{C=O})$ ,  $\delta(\text{N—H})$ ,  $\nu(\text{C—N})$ , and

$\nu(\text{C—O—C})$  in FTIR spectra of PUAs recorded as a function of increasing temperature demonstrated abrupt changes around the initial thermal decomposition temperature, making possible comprehensive studies of the thermal degradation process of PUAs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 573–579, 2006

**Key words:** polyurethanes; ionomers; pyrolysis; thermogravimetric analysis

## INTRODUCTION

Polyurethanes have extensive potential uses because the advantage of the availability of various types of diisocyanates and polyols for starting materials brings a high degree of flexibility to the molecular design. Recently, the introduction of ionic groups into polyurethanes has been extensively studied with the objective of enhancing their functionality.<sup>1,2</sup> In our previous work,<sup>3</sup> we characterized polyurethane anionomers (PUAs) containing metal and ammonium carboxylates with the aid of thermogravimetry (TG), differential scanning calorimetry, dynamic viscoelasticity measurement, and tension tests. We found that the potassium and magnesium salts of PUA showed higher tensile strength and higher elasticity than those of ordinary polyurethane elastomers because of the formation of ion clusters, although these PUA salts underwent thermal degradation more readily than did ordinary polyurethane elastomers. In the present work, we characterized the potassium and magnesium salts of PUA by TG and temperature-programmed FTIR in order to study the thermal properties of the polyurethanes in more detail.

## EXPERIMENTAL

### Sample materials

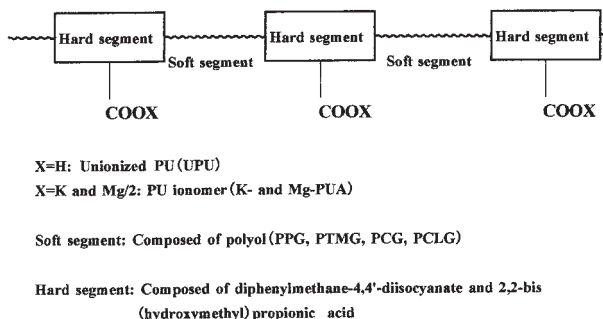
Un-ionized polyurethanes (UPU) were synthesized from 4,4'-diphenylmethanediisocyanate (MDI, 99.8 wt % purity, Nippon Polyurethane Ind. Co., Ltd.), polyols, and 2,2-bis(hydroxymethyl)propionic acid (DMPA, 98% purity, Tokyokasei Ind. Co., Ltd.) by the prepolymer method, reported previously.<sup>3</sup> Successive treatments of UPU with potassium and magnesium acetates produced the potassium and magnesium salts (K-PUA and Mg-PUA) of polyurethane anionomers (see Fig. 1). The polyols used were poly(oxytetraethylene) $\alpha,\omega$ -diol (PTMG,  $M_n = 1000$ , Hodogaya Chemical Ind. Co., Ltd.), poly(oxypropylene) $\alpha,\omega$ -diol (PPG,  $M_n = 1000$ , Mitsui Chemical Co., Ltd.), poly(carbonate) $\alpha,\omega$ -diol (PCG,  $M_n = 1000$ , Daiseru Chemical Ind. Co., Ltd.), and poly(caprolactone) $\alpha,\omega$ -diol (PCLG,  $M_n = 1000$ , Daiseru Chemical Ind. Co., Ltd.).

### Analyses

Measurement of the change in weight of the sample materials with heating was performed with a thermobalance combined with a differential thermal analyzer (Seiko Electronics model TG/DTA220) under a nitrogen atmosphere at a heating rate of 10°C/min. The samples were loaded in an Al cell.

IR spectra were measured using an FTIR microscope (JASCO model MFT-2000) equipped with a heating device (Metler model FP82HT). Chips taken from a sample material with a knife were sandwiched between two KBr plates and were compressed in a

Correspondence to: K. Matsunaga (matunaga@eng.toyo.ac.jp).



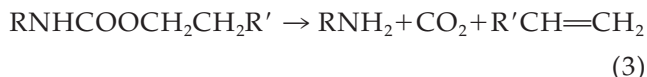
**Figure 1** Schematic representation of un-ionized and ionized polyurethane elastomers.

mold to be sealed in KBr. The spectra were recorded with 50 scans at a resolution of  $4\text{ cm}^{-1}$  and at a heating rate of  $10^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Thermogravimetric analysis

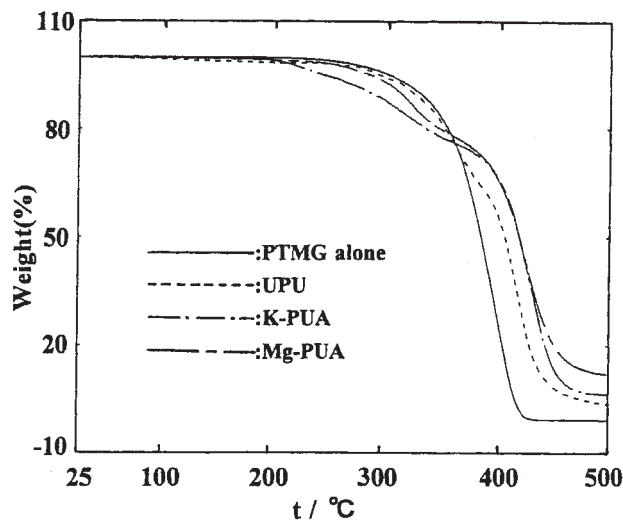
Figure 2 shows TG curves ( $25^\circ\text{C}$ – $500^\circ\text{C}$ ) observed for UPA, K-PUA, and Mg-PUA with an MDI/PTMG/DMPA mole ratio of 8 : 5 : 3 and also for PTMG alone. Among the materials studied, K-PUA exhibited the lowest initial thermal decomposition temperature,  $T_i$  (that is, the temperature at which weight loss starts) (Table I). We previously<sup>3</sup> noted the pronounced influence of potassium carboxylate on the thermal decomposition of K-PUA. It is well known that the thermal degradation of a polyurethane is initiated by dissociation [eq. (1)] and thermal decomposition [eqs. (2) and (3)] of the urethane linkage, which are accelerated under basic conditions because of the production of carbon dioxide.<sup>4,5</sup> The facile thermal decomposition of K-PUA therefore is ascribable to the acceleration of decarboxylation from the urethane linkage by potassium carboxylate.



As shown in Figure 2, PTMG reached the 95% weight value at around  $300^\circ\text{C}$ . A corresponding weight loss was observed for UPU, accompanied by a shoulder at about  $400^\circ\text{C}$ . These observations suggest that the weight loss at  $300^\circ\text{C}$  was caused by the degradation of oxytetraethylene chains, originating in the polyol, and the degradation of the resulting hard-segment residue from the MDI and DMPA components, leading to the weight loss at  $400^\circ\text{C}$ .

The effect of the structures of the polyol components on thermal decomposition was studied for K-KPU with MDI/polyol/DMPA = 8 : 5 : 3; the results are shown in Figure 3. K-PUAs synthesized with PCLG and PCG, which involve ester and carbonate bonds, respectively, were decomposed more rapidly than those synthesized with PPG and PTMG that involve an ether bond. PCG- and PCLG-based K-PUAs underwent abrupt thermal decomposition when the temperature exceeded  $T_i$ . This behavior was caused by the thermal decomposition of the soft segments. In contrast, as Table II indicates, the  $T_i$  values of the polyols alone were higher than those of the corresponding K-PUAs. Therefore, it is obvious that potassium carboxylate had a significant accelerating effect on the thermal decomposition of the soft segments. There was no significant difference between the  $T_i$  values of UPU and the corresponding Mg-PUA for any polyol used. When PCG and PCLG were used, however, the  $T_{50}$  (that is, the temperature at 50% decomposition) values of the Mg-PUAs were considerably lower than those of the corresponding UPUs, suggesting that magnesium carboxylate also accelerated the thermal decomposition of the soft segments.

In general, the thermal stability of ester-based polyols was higher than that of the corresponding ether-based polyols. Among the ether-based polyols, PTMG is known to have higher thermal stability than PPG and poly(oxyethylene) $\alpha,\omega$ -diol, though in PTMG the  $\beta$ -carbon adjacent to the ether bond is readily oxidized by atmospheric oxygen.<sup>2</sup> However, we saw that under the conditions employed in this study, the ether-based polyurethane polymers had higher thermal stability than did those based on esters. This observation clearly indicates that the presence of basic potassium carbonate in the polyurethanes resulted in a pro-



**Figure 2** TG curves of PTMG, UPU, and K- and Mg-PUA at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen.

TABLE I  
Influence of Molar Ratio of MDI/PTMG/DMPA on Thermal Decomposition of UPU and K- and Mg-PUA

Molar ratio of MDI/PTMG/DMPA	Polyurethanes	SSC <sup>a</sup> (%)	$T_i^b$ (°C)	$T_{50}^c$ (°C)
8 : 5 : 3	UPU	65.5	259	413
	K-PUA	64.6	193	417
	Mg-PUA	65.2	264	419
8 : 4 : 4	UPU	59.4	224	407
	K-PUA	58.1	184	387
	Mg-PUA	59.0	248	420
8 : 2 : 6	UPU	40.5	197	405
	K-PUA	38.7	165	377
	Mg-PUA	40.0	221	390
8 : 2 : 6	PUBD <sup>d</sup>	42.6	317	372

<sup>a</sup> Soft-segment content.

<sup>b</sup> Initial thermal decomposition temperature.

<sup>c</sup> Temperature at 50% decomposition.

<sup>d</sup> Polyurethane elastomer that 1,4-butane diol was used for instead of DMPA.

nounced influence on the thermal degradation of the soft segments originating from the polyols used as the starting materials.

## FTIR

The temperature-programmed FTIR spectra observed for K-PUA (MDI/PTMG/DMPA = 8 : 2 : 6) at selected temperatures between 100°C and 300°C are shown separately for three spectral regions in Figures 4–6: the urethane N—H stretching mode region (Fig. 4); the urethane >C=O (carbonyl) stretch region (Fig. 5); and the ether-bond stretch region (Fig. 6). The assignments of the major bands observed at 101°C are summarized

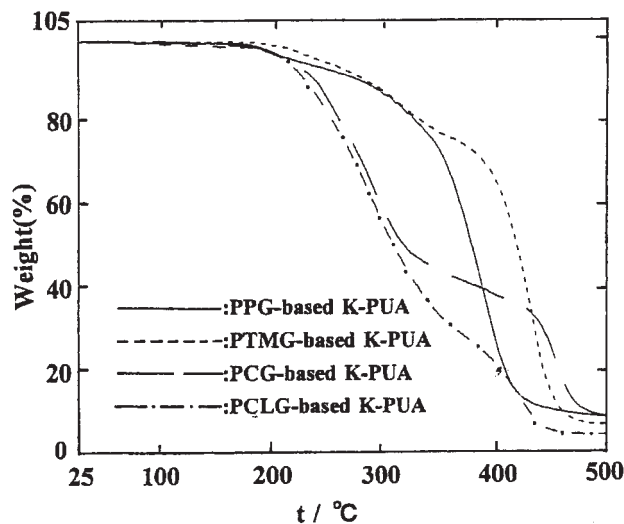


Figure 3 TG curves of a variety of polyol-based K-PUA at a heating rate of 10°C/min under nitrogen.

in Table III on the basis of recent IR studies of various types of polyurethanes.<sup>6–11</sup>

The spectral region shown in Figure 4 involves the  $\nu(\text{N—H})$  bands of urethane N—H hydrogen-bonded to ether oxygen ( $3310\text{ cm}^{-1}$ ), of urethane N—H hydrogen-bonded to urethane  $>\text{C}=\text{O}$  ( $3400\text{ cm}^{-1}$ ), and free urethane N—H without hydrogen bonding ( $3480\text{ cm}^{-1}$ ). The peak at  $3310\text{ cm}^{-1}$  was shifted to higher wave numbers with increasing sample temperature, indicating that the hydrogen bond formed by urethane N—H was gradually dissociated. At a temperature 200°C higher than the  $T_i$  determined by TG, a peak maximum was at  $3320\text{ cm}^{-1}$ . This band is attributable to amines produced by decomposition of urethane linkages [eqs. (2) and (3)]. At 250°C, the peak maximum was shifted to  $3370\text{ cm}^{-1}$ . This band was probably a result of urea formed by a reaction between the amine and isocyanate produced by the dissociation of the urethane linkages.

As shown in Figure 5, the carbonyl band of the urea linkage was observed at  $1643\text{ cm}^{-1}$  at 200°C, and absorbance was lower at 250°C. These data provide evidence that the urea N—H stretching mode was involved in the region around  $3320\text{ cm}^{-1}$  at 200°C. Additional production of isocyanate upon dissociation of urethane linkages has already been confirmed by an FTIR study.<sup>12</sup> A weak band observed around  $3370\text{ cm}^{-1}$  at 300°C probably occurred because of an O—H group produced by dissociation of urethane linkages or urea linkages that did not decompose at lower temperatures.

Figure 5 shows that the  $\nu(\text{C}=\text{O})$  ( $1714\text{ cm}^{-1}$ ) of a C=O group hydrogen-bonded to urethane N—H and that of free (i.e., non-hydrogen-bonded) C=O group

TABLE II  
Influence of Polyol Structure on Thermal Decomposition of Polyol, UPU and K-  
and Mg-PUA (MDI/Polyol/DMPA = 8 : 5 : 3)

Sample	$T_i$ (°C)				$T_{50}$ (°C)			
	PPG	PTMG	PCG	PCLG	PPG	PTMG	PCG	PCLG
Polyol alone	230	250	226	228	344	385	359	399
UPU	250	259	241	243	375	407	360	404
K-PUA	190	193	179	186	352	417	318	309
Mg-PUA	257	264	245	247	374	419	320	322

( $1732\text{ cm}^{-1}$ ) coexisted in the  $\nu(\text{C}=\text{O})$  region. No significant change was observed in this spectral region up to a temperature of  $170^\circ\text{C}$ , which was slightly higher than the  $T_i$  determined by TG. At  $200^\circ\text{C}$ , the peak maximum was at  $1732\text{ cm}^{-1}$ , and absorbance was decreased to a great extent, indicating that hydrogen-bond dissociation and thermal decomposition of the urethane linkage had occurred. At higher temperatures,  $250^\circ\text{C}$  and  $300^\circ\text{C}$ , the absorbance of  $\nu(\text{C}=\text{O})$  decreased further in a correlated manner with the decrease in  $\nu(\text{N}-\text{H})$  absorbance. In addition, significant temperature dependence was observed for a  $1595\text{ cm}^{-1}$  band (skeletal vibration of benzene ring) and a  $1528\text{ cm}^{-1}$  band (antisymmetric stretching mode of carboxylate ion + benzene-ring skeletal mode +  $\text{N}-\text{H}$  bending mode +  $\text{C}-\text{N}$  stretching mode). These results offer more evidence for the thermal decomposition of the urethane linkages. The carboxylate band at  $1420\text{ cm}^{-1}$  was clearly observed even at  $300^\circ\text{C}$ ,

although it shifted to lower wave numbers with increasing temperature. This is consistent with the ion clusters being retained. The fluidization temperature of the same sample was determined to be  $134^\circ\text{C}$  by dynamic viscoelasticity measurement. Above this temperature, the cluster ions were thought to have undergone a transition from an ordered to a disordered state and to be retained without decomposition, even when the hard segment was in a molten state.<sup>3</sup>

Figure 6 shows that the combination band of  $\delta(\text{N}-\text{H})$  and  $\nu(\text{C}-\text{N})$  at  $1223\text{ cm}^{-1}$  shifted to lower wave numbers and that a clear shoulder appeared at  $175^\circ\text{C}$ , a temperature that was much higher than the  $T_i$  ( $170^\circ\text{C}$ ) determined by TG. This shoulder increased in intensity with further increases in temperature, and at  $200^\circ\text{C}$  it was observed as a well-defined band at  $1210\text{ cm}^{-1}$ , whereas the  $1223\text{ cm}^{-1}$  band was observed as a shoulder; that is, the relationship between the intensities of the two bands was reversed. Because the dis-

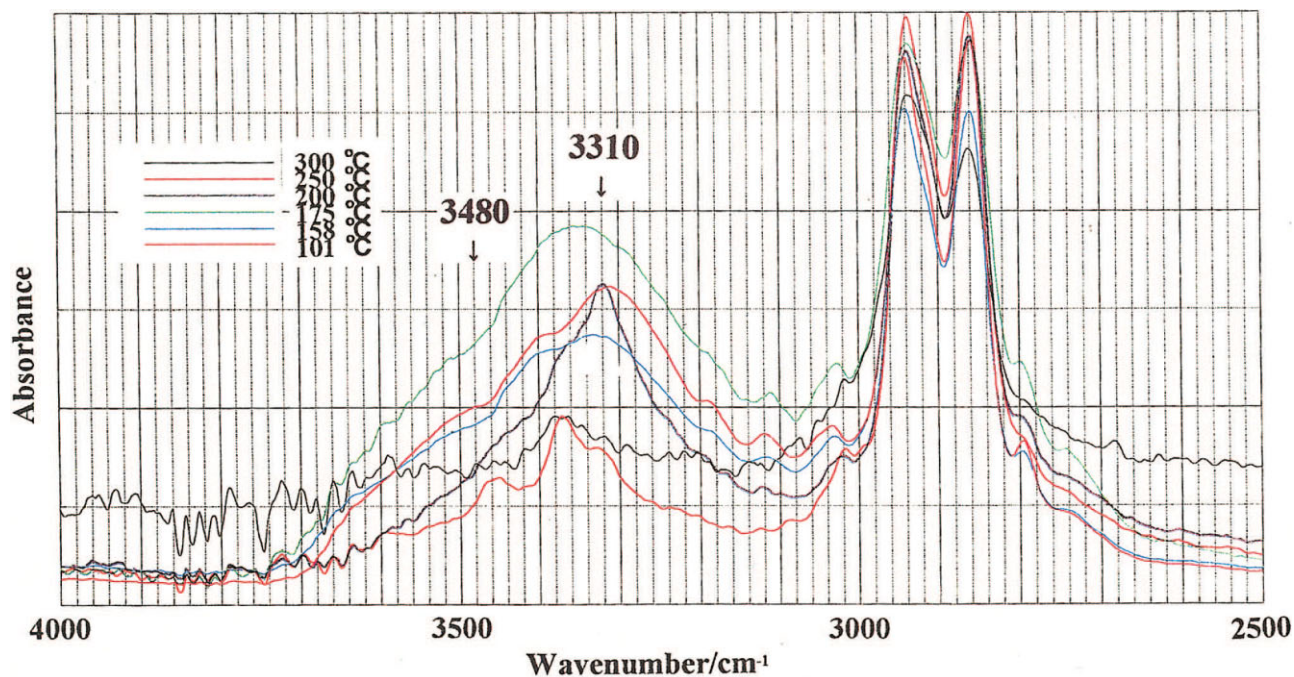
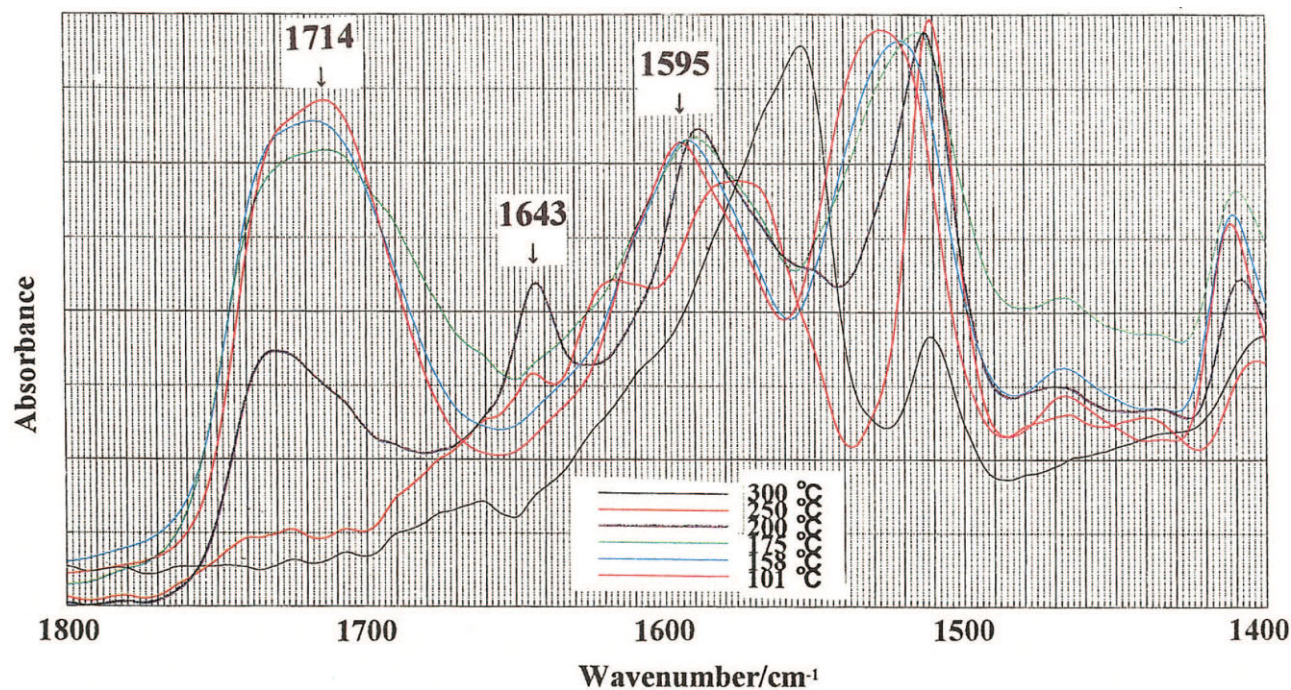


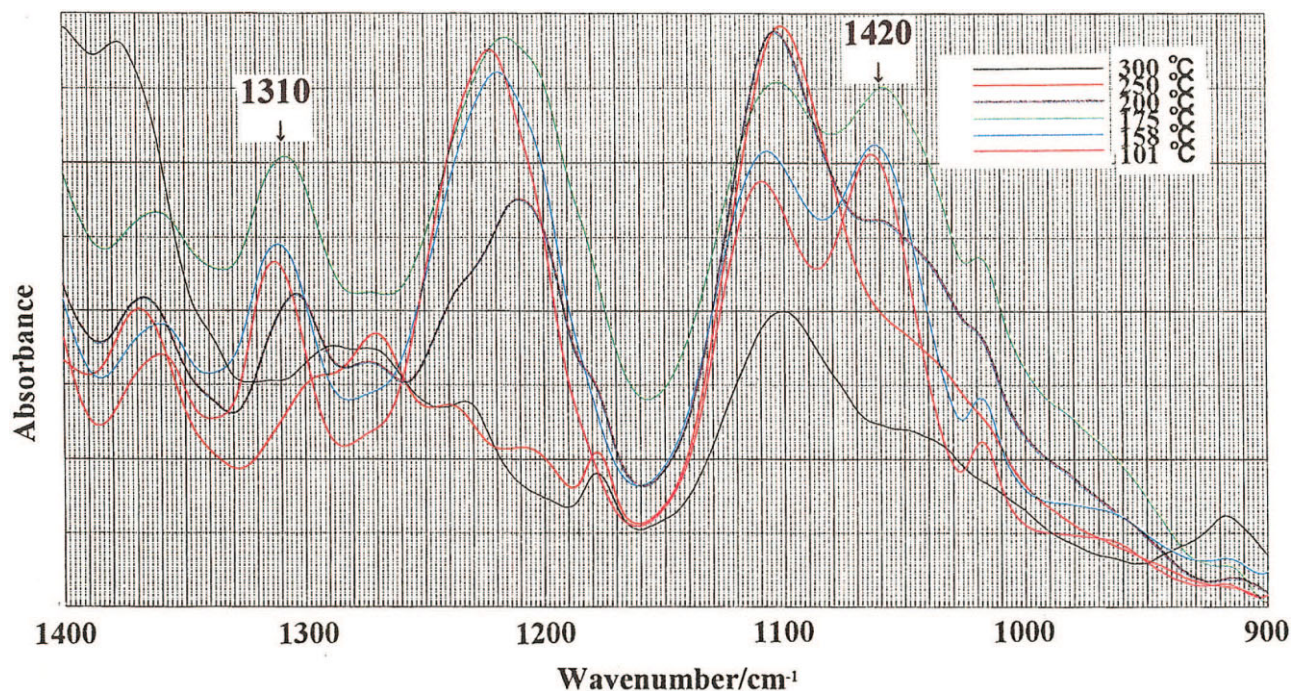
Figure 4 FTIR spectra of K-PUA in the range of  $2500\text{--}4000\text{ cm}^{-1}$  recorded from  $101^\circ\text{C}$  to  $300^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** FTIR spectra of K-PUA in the range of 1400–1800  $\text{cm}^{-1}$  recorded from 101°C to 300°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

sociation energy of the N—H bond was lower than that of the phenyl-N bond, the 1223  $\text{cm}^{-1}$  band was assignable to  $\delta(\text{N—H})$  and the 1210  $\text{cm}^{-1}$  band to  $\nu(\text{C—N})$ .

In the spectral region of the ether bond, two  $\nu(\text{C—O—C})$  bands were observed: one at 1110  $\text{cm}^{-1}$ , attributable to the free ether that was not hydrogen-bonded to urethane N—H, and the other at 1064  $\text{cm}^{-1}$ ,



**Figure 6** FTIR spectra of K-PUA in the range of 900–1400  $\text{cm}^{-1}$  recorded from 101°C to 300°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE III**  
Assignment of Absorption Bands in FTIR Spectra  
of K-PUA (MDI/PTMG/DMPA = 8 : 2 : 6)

Frequency ( $\text{cm}^{-1}$ )	Assignment <sup>a</sup>
3480	$\nu(\text{N—H})$ ; free
3400	$\nu(\text{N—H})$ ; hydrogen bonded
3310	$\nu(\text{N—H})$ ; hydrogen bonded
2940	$\nu_{\text{as}}(\text{CH}_2) + \nu_{\text{as}}(\text{CH}_3)$
2860	$\nu_{\text{s}}(\text{CH}_2) + \nu_{\text{s}}(\text{CH}_3)$
1732	$\nu(\text{C=O})$ ; free urethane carbonyl
1714	$\nu(\text{C=O})$ ; hydrogen-bonded urethane carbonyl
1595	skeletal benzene ring
1528	$\nu_{\text{as}}(\text{COO}^-) +$ skeletal benzene ring + $\delta(\text{N—H}) + \nu(\text{C—N})$
1420	$\nu_{\text{s}}(\text{COO}^-)$
1313	$\nu(\text{C—N})$
1223	$\delta(\text{N—H}) + \nu(\text{C—N})$
1110	$\nu(\text{C—O—C})$ ; free
1064	$\nu(\text{C—O—C})$ ; hydrogen bonded + urethane C—O—C group

<sup>a</sup>  $\nu$ : stretching mode;  $\nu_{\text{as}}$ : asymmetric stretching;  $\nu_{\text{s}}$ : symmetric stretching;  $\delta$ : bending mode.

assignable to hydrogen-bonded ether. These bands were markedly influenced by temperature increase: characteristically both shifted to lower wave numbers. There was also a large decrease in absorbance at 1064

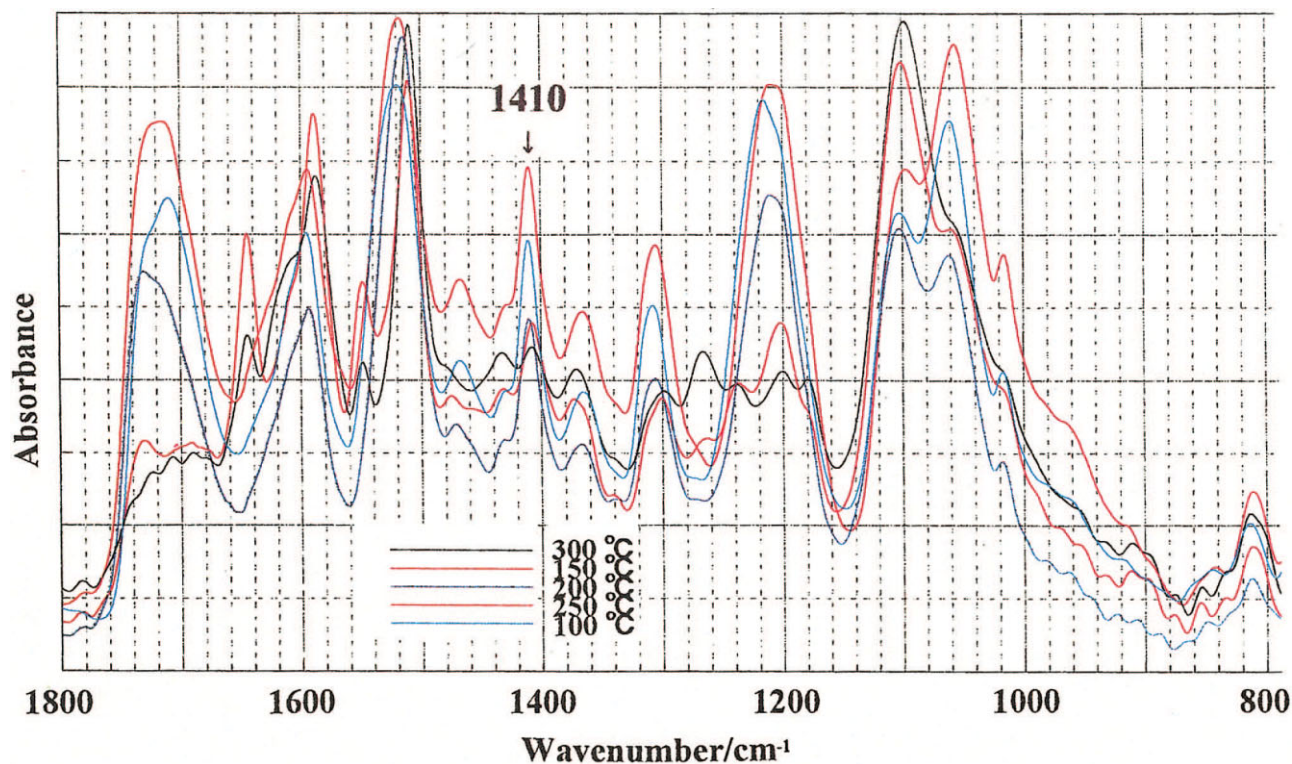
$\text{cm}^{-1}$ , with the band at  $1064 \text{ cm}^{-1}$  weakening rapidly as the temperature rose above  $175^\circ\text{C}$ , but still detectable even at  $300^\circ\text{C}$ . This band was assigned to the  $\nu(\text{C—O—C})$  of  $\text{NHC(O)—O—C}$ , as shown in Table III. The absorbance of  $\nu(\text{C—O—C})$  at  $1110 \text{ cm}^{-1}$  was much higher than that of every vibrational band of the urethane bond. This was evident from the excellent thermal stability of the ether bond under an inert gas.

If a vinyl compound is produced as shown in eq. (3), two strong  $\delta(\text{C—H})$  (out-of-plane) bands should appear at wave numbers ( $990$  and  $910 \text{ cm}^{-1}$ ) lower than  $\nu(\text{C—O—C})$ . However, no such bands were observed. This suggests that reaction 3 did not occur in the experimental conditions used in this work. A transesterification of the type shown by eq. (4) has been proposed for the degradation of a urethane linkage. This reaction, however, was difficult to confirm by FTIR.



where HX is alcohol, amine.

The temperature-programmed FTIR spectra of Mg-PUA (MDI/PTMG/DMPA = 8 : 2 : 6) closely resembled those of K-PUA described above up to  $300^\circ\text{C}$ . However, the spectra (shown in part in Fig. 7) reflected thermal stability of the polymer that was a little high. Clear bands were in the  $\nu(\text{C—N})$  region ( $1280$ –



**Figure 7** FTIR spectra of K-PUA in the range of  $800$ – $1800 \text{ cm}^{-1}$  recorded from  $100^\circ\text{C}$  to  $300^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

1330  $\text{cm}^{-1}$ ) and the  $\delta(\text{N—H}) + \nu(\text{C—N})$  region (1150–1260  $\text{cm}^{-1}$ ), even at 250°C. In addition, the absorbance of  $\nu(\text{C—O—C})$  of the free ether group was the highest at 300°C. These observations suggest that Mg-PUA has a bridge structure formed by divalent Mg ions, and the hard domain incorporates the soft phase, resulting in thermal stabilization.

The FTIR spectra of UPU (MDI/PTMG/DMPA = 8 : 2 : 6) up to 300°C essentially resembled those of K-PUA and Mg-PUA. The absorbance of  $\nu(\text{C—O—C})$  of the free ether group in UPU was the highest at 300°C, as had been observed for Mg-PUA. Up to this temperature, therefore, the soft phase underwent little thermal degradation. This is consistent with the interpretation of TG curves shown in Figure 2. The temperature-programmed FTIR spectroscopy and TG results described above show that the process of thermal degradation of PUA was promoted by ion clusters in the disordered state.

Until now, temperature-programmed FTIR spectroscopy has been used in polyurethane research only to characterize the hydrogen bonding of the urethane linkage and the phase separation structures.<sup>9,13,14</sup> The present study has demonstrated that the combined application of FTIR spectroscopy and TG is useful for studying the thermal degradation process in polyurethanes.

### CONCLUSIONS

The thermal degradation of polyurethanes containing carboxylate salts was studied by TG (25°C–300°C) and temperature-programmed FTIR spectra (100°C–300°C). The results obtained were:

1. The initial thermal decomposition temperature ( $T_i$ ) of PUA-containing carboxylate salts decreased as salt concentration increased; the carboxylate salts promoted thermal degradation of PUA.
2. K-PUAs derived from PCG and PCLG were influenced by potassium carboxylate more strongly than those derived from PPG and PTMG.
3. The IR bands of  $\nu(\text{N—H})$ ,  $\nu(\text{C=O})$ ,  $\delta(\text{N—H})$ ,  $\nu(\text{C—N})$ , and  $\nu(\text{C—O—C})$  showed an abrupt change around  $T_i$  and provided information about the degradation process.

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